

Chapter 16

Carbohydrates

SUMMARY

Section 16.1

- Biochemically important sugars usually contain five or six carbon atoms; their structure includes a carbonyl group (either the aldehyde or the ketone form) and several hydroxyl groups.
- Optical isomerism is of paramount importance in the structure of simple sugars. Most of the important sugars found in nature have the D configuration, based on the standard compound D-glyceraldehyde.
- Most sugars exist in cyclic forms with five- or six-membered rings. The cyclization process involves the carbonyl group and gives rise to another chiral center in addition to the ones already present in the sugar molecule. The two possible cyclic isomers, called anomers, are designated α and β .

Section 16.2

- Sugars can and do undergo oxidation reactions, as well as forming esters.
- Glycosidic linkages are responsible for the bonding of monosaccharides to form oligosaccharides and polysaccharides. The reaction in question takes place when one sugar hydroxyl group forms a bond with another sugar hydroxyl, usually one on an anomeric carbon. Different stereochemical forms are possible in glycosidic linkages, having important consequences for the function of the substances thus formed.

Section 16.3

- The disaccharide sucrose is common table sugar. It consists of glucose and fructose linked by a glycosidic bond.
- Lactose, found in milk, and maltose, obtained from starch, are two other common disaccharides.

Section 16.4

- Polysaccharides are formed by linking monomeric sugars through glycosidic linkages.
- Starch and glycogen are energy-storage polymers of sugars.
- Cellulose and chitin are structural polymers.
- Polysaccharides are important components of cell walls in bacteria and plants.

Section 16.5

- Sugars can be found in specific bonding arrangements in some proteins.
- Glycoproteins frequently play a role in the immune response.

LECTURE NOTES

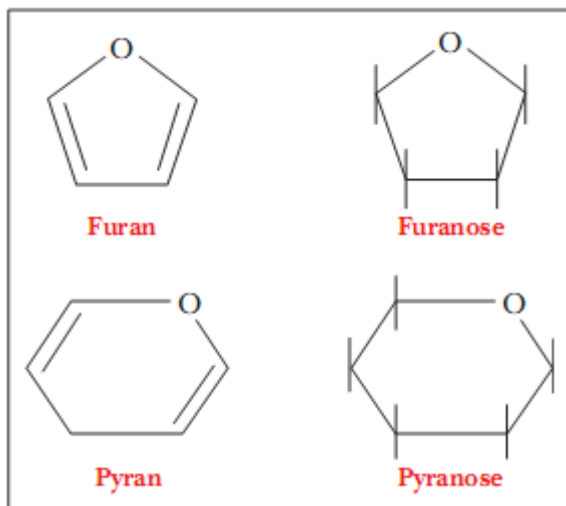
The two major topics of this chapter, the stereochemistry of monosaccharides and the nature of polysaccharides, will each take one lecture. The discussion of monosaccharides will reinforce concepts of stereochemistry introduced by amino acids. Students do have some difficulty picturing three-dimensional shapes; however, the use of models often often helps. That being said, the structure of polysaccharides involves relatively simple concepts; it is the importance of their biological role that should be stressed.

LECTURE OUTLINE

- I. Monosaccharide structures
 - A. Aldoses and ketoses
 - B. Optical isomers
 - 1. Fischer projections
 - 2. Enantiomers
 - 3. Diastereomers
 - 4. Epimers
 - C. Cyclic structures
 - 1. Hemiacetals and hemiketals
 - 2. Anomers
 - 3. Haworth projections
 - 4. Furanoses and pyranoses
- II. Monosaccharide reactions
 - A. Oxidation-reductions
 - B. Esterification reactions
 - C. Formation of glycosides
 - D. Sugar derivatives
- III. Oligosaccharides
 - A. Sucrose
 - B. Lactose
- IV. Polysaccharides
 - A. Cellulose and starch
 - B. Forms of starch
 - 1. Amylose
 - 2. Amylopectin
 - C. Glycogen
 - D. Chitin
 - E. Cell walls
 - 1. Bacterial cell walls – peptidoglycan
 - 2. Plant cell walls – cellulose, pectin, and lignin
 - F. Glycosaminoglycans
- V. Glycoproteins

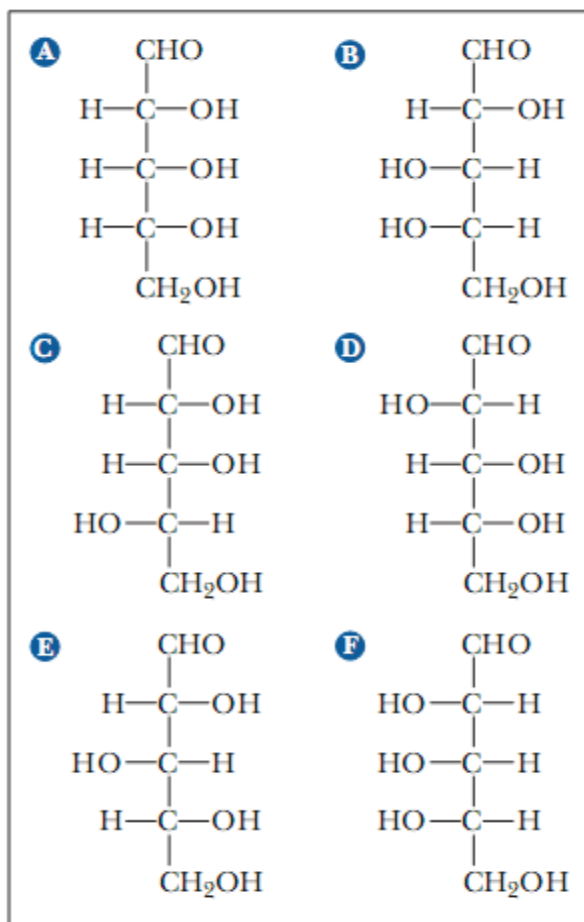
ANSWERS TO PROBLEMS**16.1 Sugars: Their Structures and Stereochemistry**

1. A polysaccharide is a polymer of simple sugars, which are compounds that contain a single carbonyl group and several hydroxyl groups. A furanose is a cyclic sugar that contains a five-membered ring similar to that in furan. A pyranose is a cyclic sugar that contains a six-membered ring similar to that in pyran. An aldose is a sugar that contains an aldehyde group; a ketose is a sugar that contains a ketone group. A glycosidic bond is the acetal linkage that joins two sugars. An oligosaccharide is a compound formed by the linking of several simple sugars (monosaccharides) by glycosidic bonds. A glycoprotein is formed by the covalent bonding of sugars to a protein.

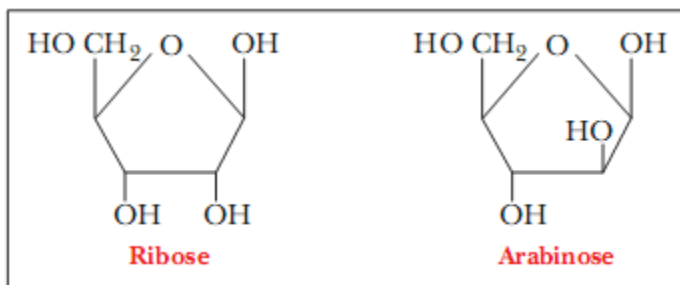


2. D-Mannose and D-galactose are both epimers of D-glucose, with inversion of configuration around carbon atoms 2 and 4, respectively; D-ribose has only five carbons, but the rest of the sugars named in this question have six.
3. All groups are aldose–ketose pairs.
4. Enantiomers are nonsuperimposable, mirror-image stereoisomers. Diastereomers are nonsuperimposable, nonmirror-image stereoisomers.
5. Four epimers of D-glucose exist, with inversion of configuration at a single carbon. The possible carbons at which this is possible are those numbered two through five.
6. Furanoses and pyranoses have five-membered and six-membered rings, respectively. It is well known from organic chemistry that rings of this size are the most stable and the most readily formed.
7. There are four chiral centers in the open-chain form of glucose (carbons two through five). Cyclization introduces another chiral center at the carbon involved in hemiacetal formation, giving a total of five chiral centers in the cyclic form.

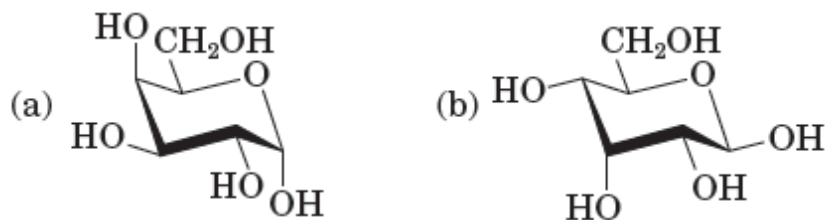
8. Enantiomers: (a) and (f), (b) and (d). Epimers: (a) and (c), (a) and (d), (a) and (e), (b) and (f).



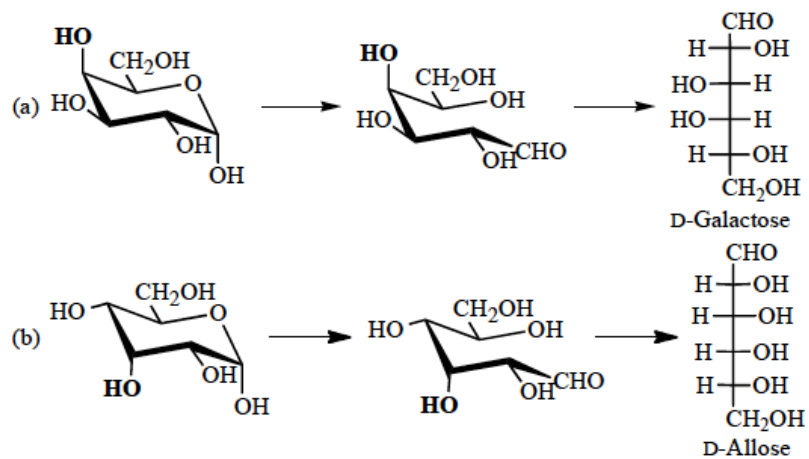
9. L-Sorbitol was named early in biochemical history as a derivative of L-sorbose. Reduction of D-glucose gives a hydroxy sugar that could easily be named D-glucitol, but it was originally named L-sorbitol and the name stuck.
10. Arabinose is an epimer of ribose. Nucleosides in which arabinose is substituted for ribose act as inhibitors in reactions of ribonucleosides.



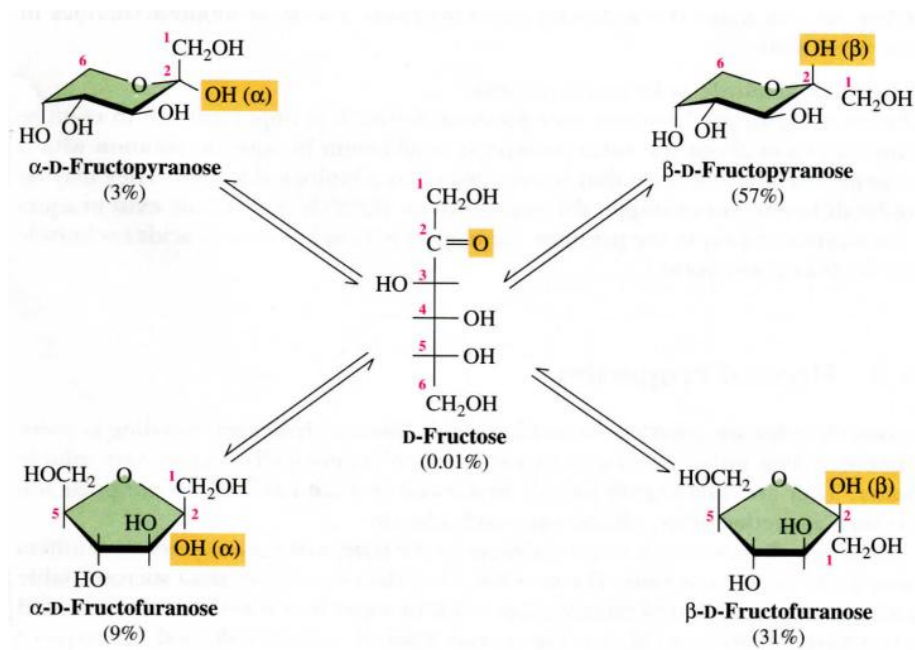
11. Converting a sugar to an epimer requires inversion of configuration at a chiral center. This can be done only by breaking and re-forming covalent bonds.
12. Two different orientations with respect to the sugar ring are possible for the hydroxyl group at the anomeric carbon. The two possibilities give rise to the new chiral center.

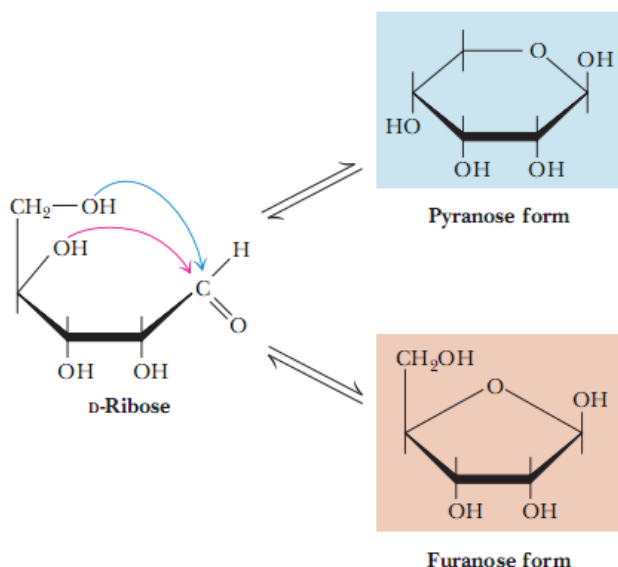


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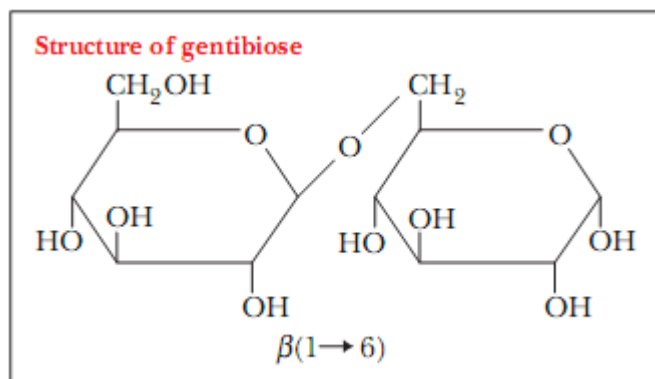


16.2 Reactions of Monosaccharides

17. This compound contains a lactic acid side chain.
18. In a sugar phosphate, an ester bond is formed between one of the sugar hydroxyls and phosphoric acid. A glycosidic bond is an acetal, which can be hydrolyzed to regenerate the two original sugar hydroxyls.
19. A reducing sugar is one that has a free aldehyde group. The aldehyde is easily oxidized, thus reducing the oxidizing agent.
20. Vitamin C is a lactone (a cyclic ester) with a double bond between two of the ring carbons. The presence of the double bond makes it susceptible to air oxidation.

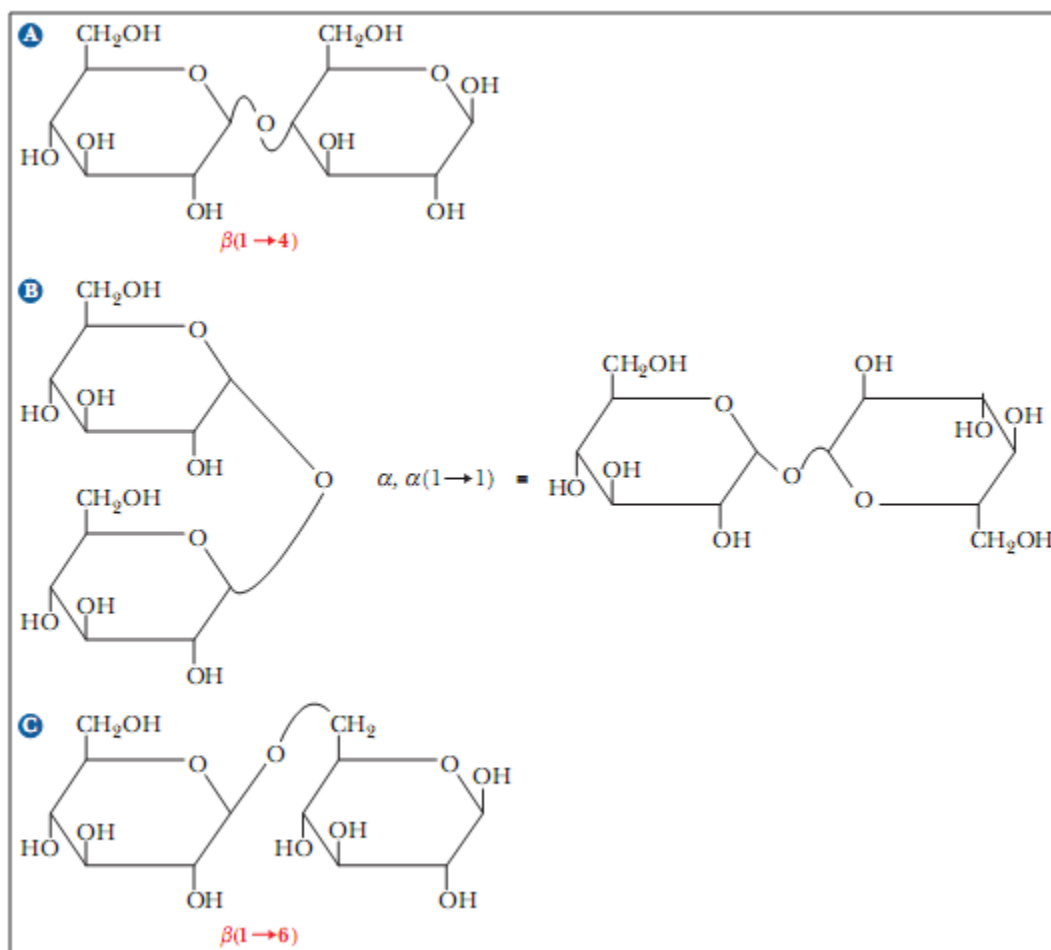
16.3 Some Important Oligosaccharides

21. Similarities: sucrose and lactose are both disaccharides, and both contain glucose. Differences: sucrose contains fructose, whereas lactose contains galactose. Sucrose has an $\alpha, \beta(1 \rightarrow 2)$ glycosidic linkage, whereas lactose has a $\beta(1 \rightarrow 4)$ glycosidic linkage.
- 22.



23. In some cases, the enzyme that degrades lactose (milk sugar) to its components—glucose and galactose—is missing. In other cases, the enzyme isomerizes galactose to glucose for further metabolic breakdown.

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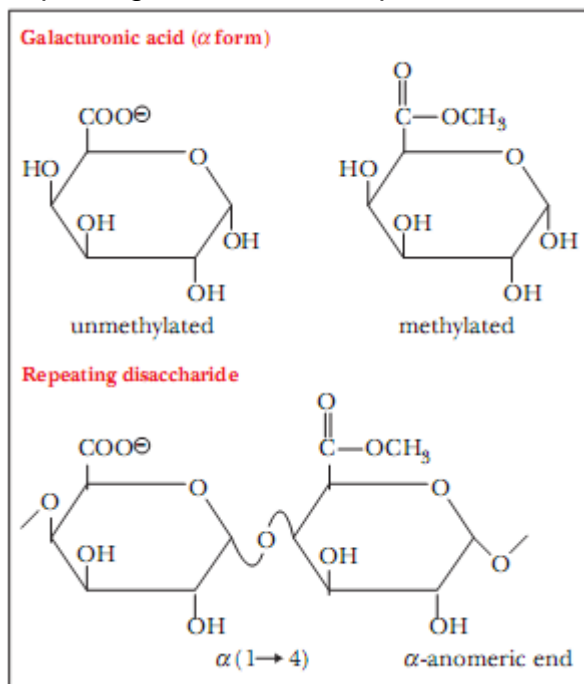


25. Milk contains lactose. Many people are sensitive to lactose and require an alternative beverage.

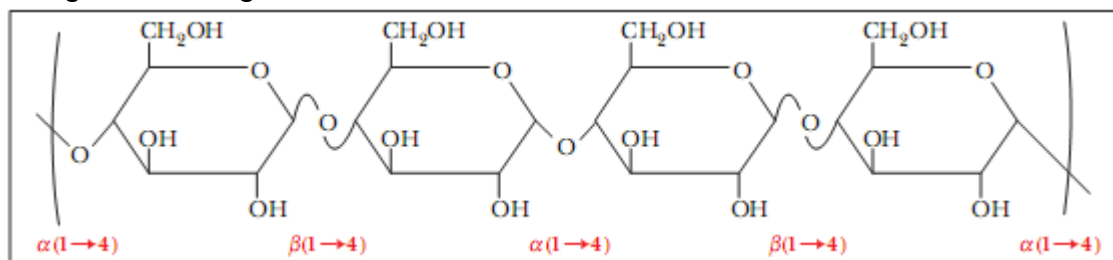
16.4 Structures and Functions of Polysaccharides

26. The cell walls of plants consist mainly of cellulose, whereas those of bacteria consist mainly of polysaccharides with peptide crosslinks.
27. Chitin is a polymer of *N*-acetyl- β -D-glucosamine, whereas cellulose is a polymer of D-glucose. Both polymers play a structural role, but chitin occurs in the exoskeletons of invertebrates and cellulose primarily in plants.
28. Glycogen and starch differ mainly in the degree of chain branching. Both polymers serve as vehicles for energy storage, glycogen in animals and starch in plants.
29. Both cellulose and starch are polymers of glucose. In cellulose, the monomers are joined by a β -glycosidic linkage, whereas in starch they are joined by an α -glycosidic linkage.

30. Glycogen exists as a highly branched polymer. Starch can have both a linear and a branched form, which is not as highly branched as that of glycogen.
31. Plant cell walls consist almost exclusively of carbohydrates, whereas bacterial cell walls contain peptides.
32. Repeating disaccharide of pectin:



33. Glucose and fructose.
34. Differences in structure: cellulose consists of linear fibers, but starch has a coil form. Differences in function: cellulose has a structural role, but starch is used for energy storage.
35. The concentration of reducing groups is too small to detect.
36. To 2500, one place (0.02%). To 1000, four places (0.08%). To 200, 24 places (0.48%).
37. This polymer would be expected to have a structural role. The presence of the β -glycosidic linkage makes it useful as food only to termites or to ruminants, such as cows and horses; these animals harbor bacteria capable of attacking the β -linkage in their digestive tracts.



38. Because of the branching, the glycogen molecule gives rise to a number of available glucose molecules at a time when it is being hydrolyzed to provide energy. A linear molecule could produce only one available glucose at a time.

39. The digestive tract of these animals contains bacteria that have the enzyme to hydrolyze cellulose.
40. Humans lack the enzyme to hydrolyze cellulose. In addition, the fibrous structure of cellulose makes it too insoluble to digest, even if humans had the necessary enzyme.
41. The enzyme β -amylase is an exoglycosidase, degrading polysaccharides from the ends. The enzyme α -amylase is an endoglycosidase, cleaving internal glycosidic bonds.
42. Fiber binds many toxic substances in the gut and decreases the transit time of ingested food in the digestive tract, so that harmful compounds such as carcinogens are removed from the body more quickly than would be the case with a low-fiber diet.
43. A cellulase (an enzyme that degrades cellulose) needs an active site that can recognize glucose residues joined in a β -glycosidic linkage and hydrolyze that linkage. An enzyme that degrades starch has the same requirements with regard to glucose residues joined in an α -glycosidic linkage.
44. Cross-linking can be expected to play a role in the structures of polysaccharides where mechanical strength is an issue. Examples include cellulose and chitin. These crosslinks can be readily formed by extensive hydrogen bonding. (See Figure 16.19.)
45. The sequence of monomers in a polysaccharide is not genetically coded, and, in this sense, it does not contain information.
46. It can be useful for polysaccharides to have a number of ends, characteristic of a branched polymer, rather than the two ends of a linear polymer. This would be the case when it is necessary to release residues from the ends as quickly as possible. Polysaccharides achieve this by having $1 \rightarrow 4$ and $1 \rightarrow 6$ glycosidic linkages to a residue at a branch point.
47. Chitin is a suitable material for the exoskeleton of invertebrates because of its mechanical strength. Individual polymer strands are cross-linked by hydrogen bonding, accounting for the strength. Cellulose is another polysaccharide cross-linked in the same way, and it can play a similar role.
48. Bacterial cell walls are not likely to consist largely of protein. Polysaccharides are easily formed and confer considerable mechanical strength. They are likely to play a large role.
49. Athletes try to increase their stores of glycogen before an event. The most direct way to increase the amount of this polymer of glucose is to eat carbohydrates.
50. Iodine is the reagent that will be added to the reaction mixture in the titration. When the end point is reached, the next drop of iodine will produce a characteristic blue color in the presence of the indicator.
51. Heparin is an anticoagulant. Its presence prevents blood clotting.
52. Glycosidic bonds can be formed between the side-chain hydroxyls of serine or threonine residues and the sugar hydroxyls. In addition, there is the possibility of ester bonds forming between the side-chain carboxyl groups of aspartate or glutamate and the sugar hydroxyls.

16.5 Glycoproteins

53. Glycoproteins are ones in which carbohydrates are covalently bonded to proteins. They play a role in eukaryotic cell membranes, frequently as recognition sites for external molecules. Antibodies (immunoglobulins) are glycoproteins.
54. The sugar portions of the blood-group glycoproteins are the source of the antigenic difference.